UCID- 18607 INTERIM REPORT TWO: GEOTHERMAL AQUATIC ECOSYSTEM PROGRAM: GEYSERS - CALISTOGA KGRA Robert R. Ireland James L. Carter CIRCULATION COPY SUBJECT TO RECALL IN TWO WEEKS April 22, 1980 This is an informal report intended primarily for internal or limited external distribution. The opinions and conclusions stated are those of the author and may or may not be those of the Laboratory. Work performed under the auspices of the U.S. Department of Energy by the Lawrence Livermore Laboratory under Contract W-7405-Eng-48.

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TABLE OF CONTENTS

		Page Number
ABSTRACT		1
INTRODUCTION		2
Involvement with Other Agencies		4
PROGRAM STATUS		7
METHODS		9
RESULTS		20
DISCUSSION	. 	, 32
CONCLUSION		38
REFERENCES		40
APPENDTY		41

LIST OF TABLES AND FIGURES

<u>Tables</u>		Page Number
1	General Water Quality Parameters	14
2	Non-Metallic Filtering Apparatus	15
3	Glass Filtering Apparatus	16
4	Organic Carbon Filtering Apparatus	17
5	Sediment Partitioning Scheme	18
,6	Analytical Chemistry Instrumentation	19
7	Summary of Field Data Sheets, Trip One, July 1979.	21
8	Summary of Field Data Sheets, Trip Two, October 1979.	21
9	Summary of Field Data Sheets, Trip, Three February 1980.	21
10	Anions	26
11	Dissolved Trace Elements	27
12	Sediment: HCl Extract of Size Fractions 850 μ - 590 μ and 590 μ - 250 μ .	28
13	Sediment: HCl Extract of Size Fractions 250 μ - 149 μ and <149 μ .	29
14	Particulate Trace Elements: HCl Extract	30
15	Composition of Unit 12 Cooling Water	31
Figures		•
1	Big Sulphur Creek Sampling Locations	12
2	Field Data Sheet	13
3	Ammonia	22
4	Sulfate	23
5	Boron	24
6	Potaccium	25

ABSTRACT

Preliminary data are presented from several quarterly sampling trips in the Big Sulphur Creek area of the Geysers-Calistoga KGRA. Elemental constituents of the water column and acid-extracted sediments are shown in relation to sampling sites located on or near natural thermal tributaries, mine tailings, and geothermal power plant units. Selected constituents, such as ammonia, boron, potassium, and sulfate, show enrichment in both natural geothermal waters and in cooling tower waters and emissions. It is shown that significant influxes of elements are contributed by geothermal units. The most probable source is cooling tower drift aided by rainfall mobilization. Some elements, such as arsenic, appear to preferentially accumulate in the sediment but are purged rapidly by the natural scouring of high winter flows. Other geochemical markers remain essentially unchanged. The interpretation and significance of mass chemical input and flux within the aquatic ecosystem will be presented at a later time.

INTRODUCTION

Never has the need been more apparent for the development of alternate energy sources. One of the most visible of these is geothermal energy. Though generally regarded as an environmentally clean energy producer, it nonetheless, like all commercial endeavors, contributes its share of potential environmental problems.

The Geysers-Calistoga KGRA in Northern California is currently the largest producer (502 MWe as of March, 1979) of geothermal energy in the world (Michler, 1979). The amount of construction and development upon the primary watershed, the Big Sulphur Creek drainage, is impressive. Fifteen operational units are situated in an area of steep and complex terrain. The first hand observer can easily identify the key environmental issues of concern: erosion, cooling tower drift, H₂S, and noise.

Not so apparent is the long-term cumulative impact to terrestrial and aquatic ecosystems. Our geothermal ecology group has addressed themselves to this issue for the past year. This report represents a summary of the progress to date for the aquatic segment of the ecology program.

The rationale of the aquatic ecology program has previously been stated (Ireland, 1979). We are primarily concerned with the long-term cumulative impacts upon the aquatic ecosystem. Erosion and cooling tower drift are the chronic sources of development-related influences to the natural system. The degree of input to the ecosystem from non-developmental sources such as natural hot springs, abandoned mercury mines, and other sources are unknown and have not been quantified.

Fundamental to understanding the environmental consequences of geothermal development is the procurement of information concerning transfer, cycling and the accumulation of potentially toxic trace elements, such as Hg, As, NH₃, within the watershed.

The mechanisms and dynamics of the ecosystem are a function of the relationships between the physical, chemical and biological characteristics of the waters and sediments. These relationships determine the suitability of the habitat. In taking only grab samples of water, one is merely freezing a moment in time within the streamflow. But by directing our studies to the chemical interrelationships between sediment and water, we are taking advantage of sediment as a natural sink. It becomes an integrator of the chemical pulses over a longer time course than flowing water.

Most of the literature regarding sediment has considered only its physical characteristics. Such studies yield excellent information about erosional input, mass movement of fine particles and streambed composition. Another approach is the delineation of the chemical nature of the sediment. This provides information about the accumulation of nutrients and potentially toxic trace elements, their rate of accumulation, the manner in which elements are sorbed, and their potential for release.

By integrating data relative to the physical and chemical properties of sediment and water, and the biological systems involved, we can gain insight into many questions, such as: What is the quantifiable input from natural sources versus geothermal power plant sources? What elements are still bioavailable and which are not available to the biota? How is the food chain being affected from primary producers to rainbow trout? What will be the physical and chemical contribution of several new proposed units to the drainage? Is there a natural buffering capacity within the aquatic ecosystem which is being strained?

Various agencies and institutions have conducted studies of a short term and/or rather limited scope within the Geysers KGRA. None have employed the type of chemical ecology program we have initiated. Nor have they considered what the long-term cumulative effects might be. Inventories of insects and fish species and bioassays at unrealistically high concentrations of contaminants are of only limited value. The study of the chronic low-level type of accumulating contamination is ultimately the more realistic approach. In the long run, studies directed to elucidate this perspective will answer far more questions about the quality of the ecosystem. This type of information gathering will

also contribute significantly to the rather small body of knowledge concerning the effects of geothermal energy upon aquatic ecosystems.

Our studies in the Big Sulphur Creek watershed address themselves to the unique environmental problems of cooling tower drift and erosion in this complex terrain. These studies can also be considered of a generic nature in that they represent opportunities for us to learn more about the general environmental impacts of diverse geothermal operations. Additionally, this study will increase our understanding of the mobility, partitioning, and fate of potentially toxic elements, such as mercury and arsenic, which are common environmental concerns in other energy technologies.

INVOLVEMENT WITH OTHER AGENCIES

1. Pacific Gas and Electric

We have established an excellent working relationship with the aquatic biology team at PG&E. They are extremely interested in our chemical ecology approach inasmuch as they have been conducting erosion and fisheries resources studies within the Geysers KGRA (Price, 1972). Since we have taken care to physically classify the stream bed composition, we will be able to expand the breadth of our studies by comparison to theirs. Our chemical characterization studies integrated with their particle-size characterization will provide a unique, complementary blend of physicochemical data within the aquatic environment. And on the basis of their years of collecting data, we will be able to extrapolate chemical movement to previous years and to fisheries inventories. We are currently in the process of establishing a common computer data base for such purposes.

2. University of California, Berkeley

We have also planned to share data with a group at the University of California in Berkeley. This group has been interested for years with the unusual nature of the invertebrate community in the Little Geysers Creek area (Resh, 1979).

Both of us are hopeful that the generation of nutrient and geochemical information in this area will provide clues as to why this is an unique and diverse community.

3. California Energy Commission

We have also become actively involved in a formalized group of agencies headed by the California Energy Commission. The objectives of this group are to evaluate cumulative impacts upon the aquatic ecosystem, assess the effectiveness of mitigation procedures, and coordinate efforts to reduce redundancy, curb expenditures and promote information flow (see Appendix 1). We have been chosen as the leaders in the sediment area because of our acknowledged expertise and ongoing program. Everyone involved is interested in our approach to elemental input and cycling and all agreed it would enhance the fundamental understanding of the ecosystem dynamics.

The advantage to us of belonging to this group are that we will be granted access to a much wider variety of data than we could generate ourselves. Personal and scientific liaisons are being established which could prove to be valuable.

Sampling sites have been coordinated with ours to provide a more integrated biological and chemical data base. Information at given sites which will be blended include physical and chemical parameters of water and sediment, fish diversity, biomass estimates, species movements within the major streams and tributaries, and data on abundance and diversity of benthic invertebrates.

The CEC group is interested in all three of the watersheds in the Geysers KGRA. The Big Sulphur Creek watershed, where LLL is now, is the area of all current energy production. The Putah Creek watershed, an area of recent building, will have two power units come into operation in late 1980 or 1981. The Kelsey Creek drainage is undeveloped so far but some units have been proposed and are undergoing consideration at this time.

The value of this large scale planning to us is that we have input into the design and rationale of the proposed sites and data gathering prior to conduct-

ing our research there. When we receive funding to channel LLL resources into the next watershed, we will be moving into an already coordinated program. As such, it will make our transition more smooth and efficient.

PROGRAM STATUS

We have currently completed four quarterly field trips to the Big Sulphur Creek area. Our first venture was in April 1979. This was designed to be a reconnaissance trip to identify sampling locations. At that time, we also took the opportunity to introduce ourselves to local personnel from PG&E and Union Oil and to familiarize them with our proposed program.

Our next field trip, considered number one, was in late July 1979. This was a period of low flow. One might expect a maximum accumulation at this time. Trip two was conducted in October 1979. Our intent was to go immediately after the first rains. The rationale was to measure the amount of mobilized constituents entering the aquatic environment from runoff. Trip three was conducted in February 1980. We wished to see the effect of the natural flushing of the watershed upon the trace elemental loading. Trip four will be in May or June after the rains have subsided and groundwater flows have stabilized. This will be a gauge of the natural baseline prior to a summer of low flow and deposition.

We have established an orderly flow of data from the analytical instrumentation to the computer for several reasons. First, our main tool for detecting trace elements is the ICPOES. This instrument is capable of detecting approximately twenty five elements in a complex matrix at environmental levels, often parts-per-billion. Extensive use of our computer facilities was required for our extremely large number of data bits in order to change from instrumentally observed number to corrected numbers.

We also spent a great deal of time on the organization of our data base with an eye toward the statistical manipulation of the numbers. This will facilitate the ease with which we can assess interactive chemical dynamics and multi-element correlations.

Thirdly, we are preparing our data base to be more receptive to the integration of data from other institutions. This primarily means PG&E, as mentioned previously. We are certain this effort will be repaid with the capacity to blend our chemical data with physical sediment data and with biological data from fisheries and benthic invertebrate surveys.

METHODS

The following text and tables represent a summary of our methods. Of primary importance is the recognition that we are dealing with elemental concentrations at the trace level. Therefore, all our work, both field and laboratory, is done with utmost care to avoid any contamination.

Before initiating our program, we conducted a critical literature review.

After this search, we chose the best methods applicable to our study.

I. Field Methods

Big Sulphur Creek flows through steep and complex terrain. Therefore, we are unable to drive to the sampling location. We do, however, park a mobile laboratory and four-wheel drive truck as close as possible, then utilize back-packs to transport our equipment. Sampling locations are shown in Fig. 1.

At each sampling site, a field data sheet is employed to record information. This is shown in Fig. 2.

A variety of standard water quality parameters are taken at each site in addition to samples. These are listed in Table 1.

Water samples for analytical characterization are treated individually in accordance with their fate. Specific precautions are taken regarding apparatus, type of filter, type of storage bottle, preservation, and mode of analysis. All field filtering is accomplished by means of a standard tire pump capable of pulling one atmosphere. Three separate types of filters are used. These are presented in Tables 2, 3, and 4 with the purpose and an explanation.

Sediments are collected in the field using a long handled PVC scoop. The sample is presieved through a 2000 μ nylon screen. The gravel which does not pass the screen is placed in a bag, weighed, then discarded.

The < 2000 μ fraction is taken back to the laboratory for further particle size fractionation.

Four other separate sediment samples are taken: three 250 cc aliquots in poly bottles for future dry screening and one 250 cc aliquot in a glass bottle for organic carbon determination. The fate of the sediment samples is shown in Table 5.

II. Laboratory Methods

A. Water

Aliquots of unfiltered water are digested in platinum crucibles using HNO₃-HF. These prepared sub-samples are then analyzed for trace elements using the inductively-coupled plasma optical emission spectrometer (ICPOES). Aliquots of filtered water require no digestion and are also analyzed by the ICPOES. See Table 6 for a listing of the analytical instrumentation.

Mercury is analyzed by the atomic absorption cold vapor hydride method.

Arsenic is currently being analyzed by ICPOES, but shortly we will be using a

Princeton Polarograph employing the method of cathodic stripping voltammetry.

Anion samples are analyzed with an ion chromatograph which uses a carbonate buffer as the eluant.

The Gelman GN-6 filters are extracted in 0.5 N HCl for 18 hours. The acid extract is submitted for analysis by ICPOES. The filters are then digested with HNO₃-HF for residual elemental analysis.

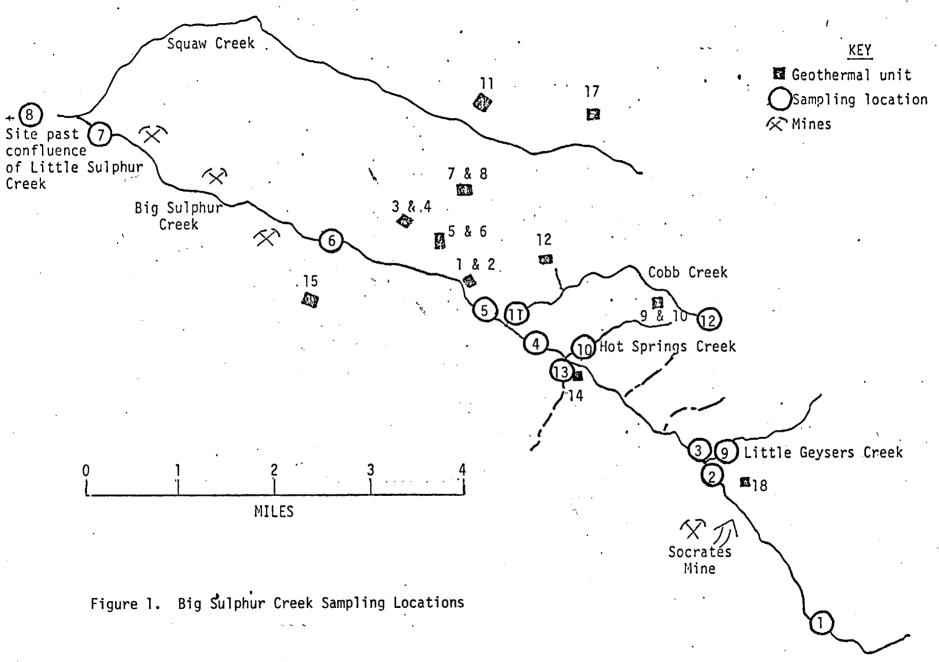
B. Sediment

Sediment from each site is wet sieved in the laboratory using nylon screens mounted in polycarbonate holders. Water for the wet sieving is collected at each site at the same time as the sediments. A complete description of our sediment scheme is represented in Table 5.

All sediment fractions less than 850 μ are leached with 0.5 N HCl. The sediment fraction < 149 μ is sequentially extracted (Ireland, 1979).

Three separate composite sediment samples are used for particle size fractionation via dry screening. The separate sample taken for organic carbon is analyzed on an Oceanography International Total Carbon Analyzer.





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Table 1. General Water Quality Parameters.

Parameter	Rationale	Equipment
Temperature	General information. May detect covert hot spring addition to stream or tributary.	Field thermometer
рН	General information. Important for chemical speciation and biological conditions.	Hach pH Kit. Brom Thymol blue indicate Colorimetric.
Conductivity	Measure of dissolved ion (electrolyte) load in water column.	Hach Conductivity Meter. Field Model 2510.
Dissolved Oxygen	Possible detection of localized reducing conditions. Important biologically.	Hach DO Kit. Winkler Method. Colorimetric.
Turbidity	Measure of clarity. Correlates to suspended solids.	Hach Turbidimeter. Model 2100 A.
Alkalinity	Measure of HCO_3^- and CO_3^- species in water. These are generally the predominant inorganic ligands in clean freshwater systems and affect complexation and precipitation.	Hach Alkalinity Kit. Bromcresol green indicator. Colori- metric.
Flow	Needed to standardize elemental concentrations for nutrient movement, elemental flux, and mass loading	Marsh-McBirney Model 201 M Flow Meter.

Table 2. Non-metallic filtering apparatus.

Filter & apparatus	Filtering purpose	Explanation			
Gelman GN-6 nitrocellulose , filter 0.45 μ	Dissolved trace elements	Dissolved is operationally defined as 0.45 μ . Water samples are stored in acid washed poly bottles and acidified with HNO ₃ at the site.			
Gelman all-polypropylene filtering apparatus	> Anions	Samples for anion analysis are stored, without acid addition, in glass reagent bottles. They are also covere with aluminum foil to prevent microbial growth.			
	Particulate trace elements	Filtered solids deposited on the membrane are later (1) leached with 0.5 N HCl, then (2) totally dissolved with HNO ₃ -HF to gain information on particulate elemental transport.			

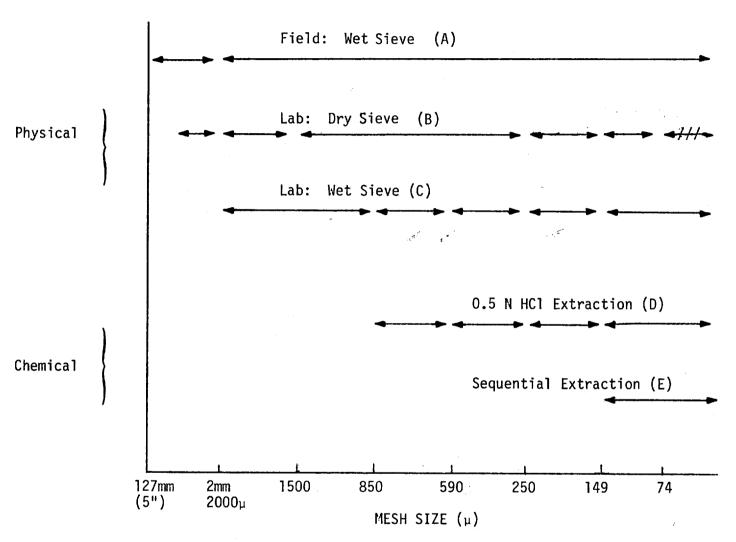
Table 3. Glass filtering apparatus.

Filter & apparatus	Filtering purpose	Explanation
Gelman GF/AE glass fiber filter	Total suspended solids (TSS)	Dried, preweighed filter used. In lab, filter is redried and reweighed. Weight difference is TSS in mg/l.
Millipore stainless steel filter support	Mercury	An aliquot of filtered water is prepared especially for Hg analysis by acid addition and H_2O_2 . This helps maintain the element in the Hg ⁺⁺ nonvolatile state. Sample is stored in a acid washed poly bottle.
	NH ₃	An aliquot for $\rm NH_3$ determination is stored separately with addition of $\rm H_2SO_4$. All $\rm NH_3$ samples are analyzed within 10 h using an Orion specific ion $\rm (NH_4^+)$ electrode and an Orion 407 meter.

Table 4. Organic carbon filtering apparatus.

precombusted: 1. 25 mm GF filters 2. Filter holders 3. Syringes 4. Collection bottles 5. Ampules Dissolved organic carbon Dissolved organic carbon Dissolved organic carbon Particulate organic carbon Particulate organic carbon Particulate organic carbon Dissolved organic carbon Dissolved organic carbon The system. Furthermore, huming and fulvic acids in the water column play a definite role in the complexation and transport of elements. Both total and dissolved water samples, and the filter are placed into appropriate ampulation the mobile lab. Later they are thawed and	Apparatus	Sample purpose	Explanation
	precombusted: 1. 25 mm GF filters 2. Filter holders 3. Syringes 4. Collection bottles	Carbon Dissolved organic carbon Particulate organic carbon	is a measure of the biological and chemical oxygen demand on the system. Furthermore, humic and fulvic acids in the water column play a definite role in the complexation and transport of elements. Both total and dissolved water samples, and the filter are placed into appropriate ampule then frozen immediately with dry ice in the mobile lab. Later they are thawed and analyzed bychemical oxidation

Table 5. Sediment partitioning scheme.



- (A) The < 2000 μ sample is brought back to the lab and wet sieved with small mesh screens (C). After the fractions have been dried and weighed, they are then used in extractions (D) and (E).
- (B) Dry sieving is employed for particle size fractionation.

NOTE: PG&E dry sieves their samples in their lab into 16 size categories from 127 mm (5") on down. They employ the same cutoff sizes we do from 1500 μ to 74 μ .

//// is Pipette analysis.

Table 6. Analytical Chemistry Instrumentation.

Analysis for:	Instrument
Total, dissolved and particulate trace elements	Inductively-coupled plasma optical emission spectrometer: ICPOES
Mercury	Atomic absorption (cold vapor hydride method)
Arsenic	Cathodic stripping voltammetry using Princeton Polarograph; ICPOES
Anions	Ion chromatograph
Organics	Oceanography International Total Carbon Analyzer
Ammonia	Orion Specific Ion Meter Model 407 and Specific Ion (NH ₄ +) electrode

RESULTS

Summaries of the information recorded on the field data sheets are presented in Tables 7, 8, and 9. Ammonia measurements must be taken within twelve hours after sampling or the results may be invalid. No ammonia is recorded from trip one due to electrode failure.

Histograms of constituents of known geothermal importance are presented in relation to their sampling locations (13 is an intermittent sediment basin and, therefore, is not plotted). These dissolved constituents are found in elevated levels in the natural thermal waters, i.e., Little Geysers Creek and Hot Springs Creek, and also in the power plant cooling tower water (see Table 15). The graphical representations include:

Figure 3: Ammonia

Figure 4: Sulfate

Figure 5: Boron

Figure 6: Potassium

Other preliminary data are presented as the range of concentrations found among the thirteen sampling locations. These tables include:

Table 10: Anions

Table 11: Dissolved trace elements

Table 12: Sediment: HCl extract of size fractions 850 μ = 590 μ and 590 μ = 250 μ

Table 13: Sediment: HCl extract of size fractions 250µ - 149µ,<149µ

Table 14. Particulate Trace Elements: HCl extract

Table 7. Summary of Field Data Sheets; Trip 1; July and August 1979.

itation	Date (7/79- 8/79)	Time of day	Tempera: Air	ture (°C) Water	Dissolved oxygen (mg/l)	рH	Alkalinity (as ppm CaCO ₃)	Conductivity (µmhos/cm)	Turbidity (JTU)
1	8/4	1845	23.0	21.0	10.0	7.70		310	
2	8/4	1600	24.5	30.5	7.0	7.40		480	0.68
3	8/4	1230	28.0	37.0	6.0	7.75	14	395	0.55
4	7/31	1225	35.5	30.0	8.0	7.4	17	420	0.24
5	8/2	1613	32.5	26.0	8.0	7.65	15	450	0.35
6	8/3	1215	29.0	25.0	, 8,0	7.60	10	560	0.73
7	8/2	1135	29.0	24.0	8.0	7.55	11	540	0.66
8	7/30	1610	38.0	29.5	9.0	7.40	10	320	0.32
9	8/4	1700		50.0				405	0.35
10	7/31	1705	30.5	32.5	2.5	7.10	19	520	
11	8/1	1205	33.5	21.0	9.0	7.70	13	370	0.12
12	8/4	0745	12.0	13.0	8.0	7.20	6	165	0.12

Table 8. Summary of Field Data Sheets; Trip 2; October 1979.

Station	Date (10/79)	Time of day	Temperature Air	(°C) Water	Dissolved axygen (mg/1)	рН	Alkalinity (as ppm CaCO ₃)	Conductivity (umhos/cm)	Turbidity (JTU)	NH ₃ (mg/1)	Flow (cu. m/sec)
1	23	1115	15.1	13.9	9.0	7.55	4.0	130	5.4	< 0.01	0.4599
2	25	1600	17.0	13.0	6.0	7.4	4.0	105	18.0	< 0.01	2.1247
3	25	1440	16.0	13.0	10.0	7.3	3.0	105	20.0	< 0.01	1.4483
4 '	24	1405	15.0	15.0	10.0	7.4	10.0	320	2000.0	0.020	0.3434
5	26	1000	9.0	12.0	9.0	7.7	6.0	195	9.8	0.016	1.4413
6	25	1115	19.0	14.0	9.0	7.3	2.0	200	87.0	0.127	very high
7	26	1315	15.0	13.0	10.0	7.7	6.0	250	9.5	0.130	1.6925
8	26	1500	17.0	15.0	9.0	7.5	6.0	220	7.8	0.035	3.9768
9	25	17.0	15.0	20.0	8.0	7.2	6.0	200	40.0	0.038	0.0785
10	24	1240	16.0	23.0	5.0	7.4	13.0	540	8.3	0.31	0.0029
11	24	0940	16.0	14.0	9.0	7.7	9.0	310	1.9	0.011	0.0393
12	23	1450	13.0	12.0	9.0	7.4	5.0	165	0.45	< 0.01	0.0285
. 13	23	1725	13.8	14.0	9.0	-7.6	4.0	180	2.6	< 0.01	0.0200

Table 9. Summary of Field Data Sheets; Trip 3; February 1980.

Station	Date (2/80)	Time of day	Tempera Air	ature (°C) Water	Dissolved oxygen (mg/l)	рН	Alkalinity (as ppm CaCO ₃)	Conductivity (µmhos/cm)	Turbidity (JTU)	NH ₃ (mg/1)	Flow (cu. m/sec)
1	13	1425	9.0	6.5	10.0	7.5	6.0	70	1.0	< 0.01	0.0738
2	13	1030	7.5	5.5	13.0	7.35	8.0	110 .	0.51	< 0.01	0.092
3	13	0911	7.5	9.5	11.0	7.5	8.0	110	1.0	0.03	0.173
4	14	0925	8.0	12.5	10.0	7.8	9.0	290.	0.9	0.0235	0.268
5	11	1500	11.0	12.0	11.0	7.6	10.0	220	0.77	0.0162	0.681
6	12	0925	9.0	11.5	10.0	7.65	9.0	300	4.3	0.177	0.880
7	11	1250	12.5	11.0	J 1.5	7.9	10.0	365	2.7	0.15	1.033
8	14	1510	10.5	11.0	12.0	7.9	10.0	305	1.3	0.0285	2.788
9	13	1207	10.5	22.0	. 8.0	7.02	8.0	165	3.8	0.056	0.057
10 ,	14	1055	8.5	18.5	9.0	7.7	13.0	360	1.1	0.0580	0.032
31	12	1430	10.5	11.0	10.0	7.70	8.0	240	0.67	< 0.01	0.122
12	12	1206	7.5	9.0	11.0	7.4	6.0	50	0.24	< 0.01	0.016
13	14	1240	9.0	9.5	11.0	7.46	6.0	150	1.6	< 0.01	0.015

Figure 3. Ammonia

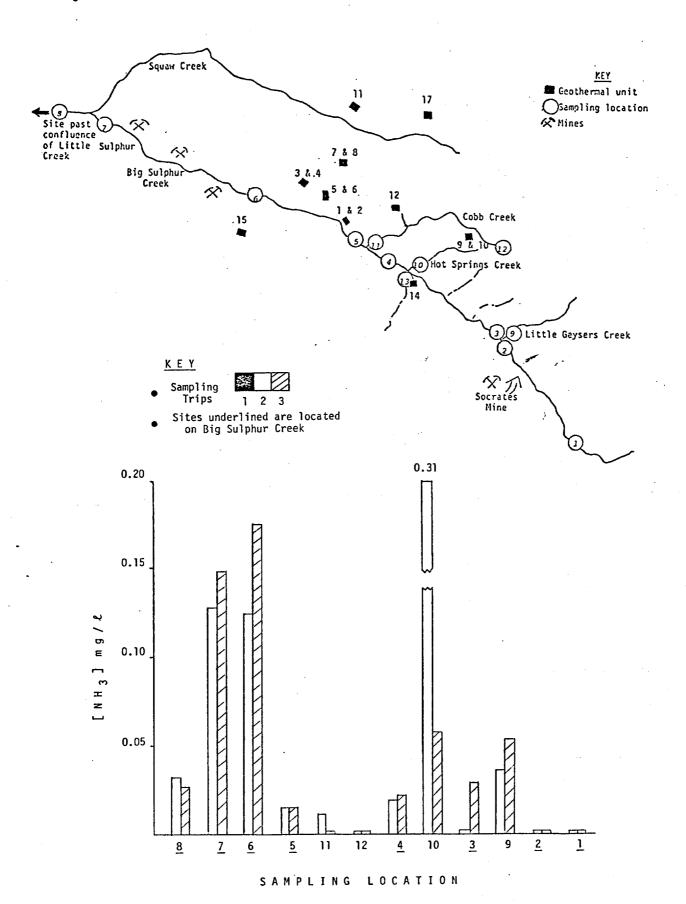


Figure 4. Sulfate

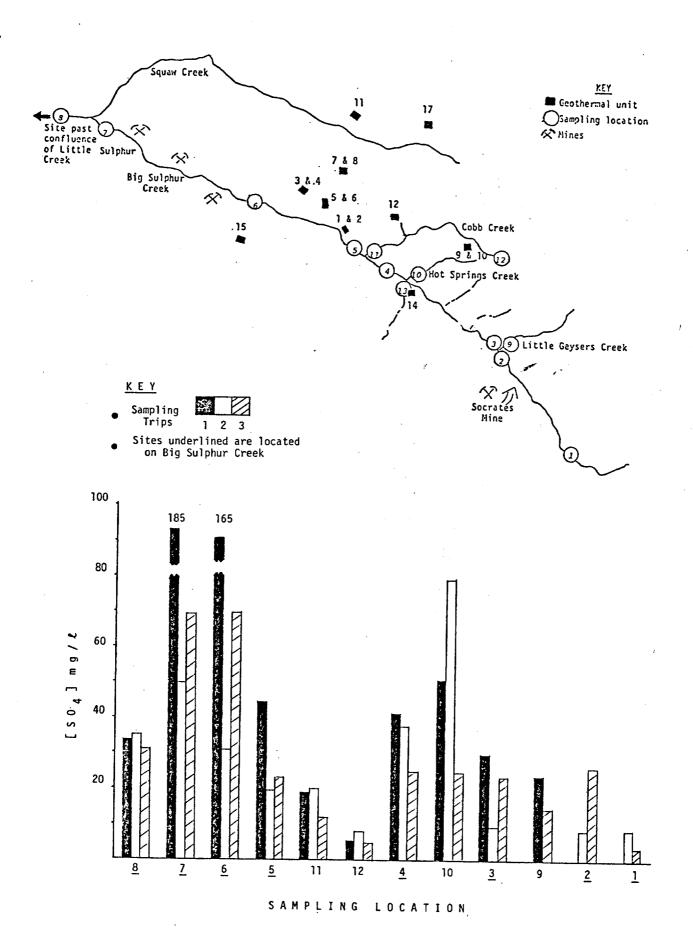


Figure 5. Boron

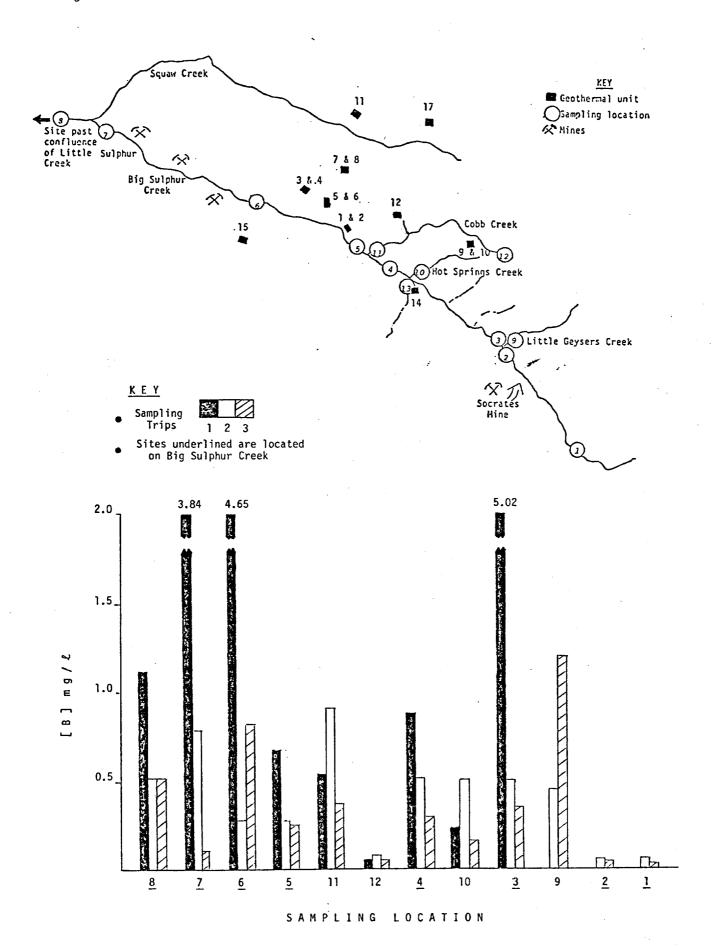


Figure 6. Potassium

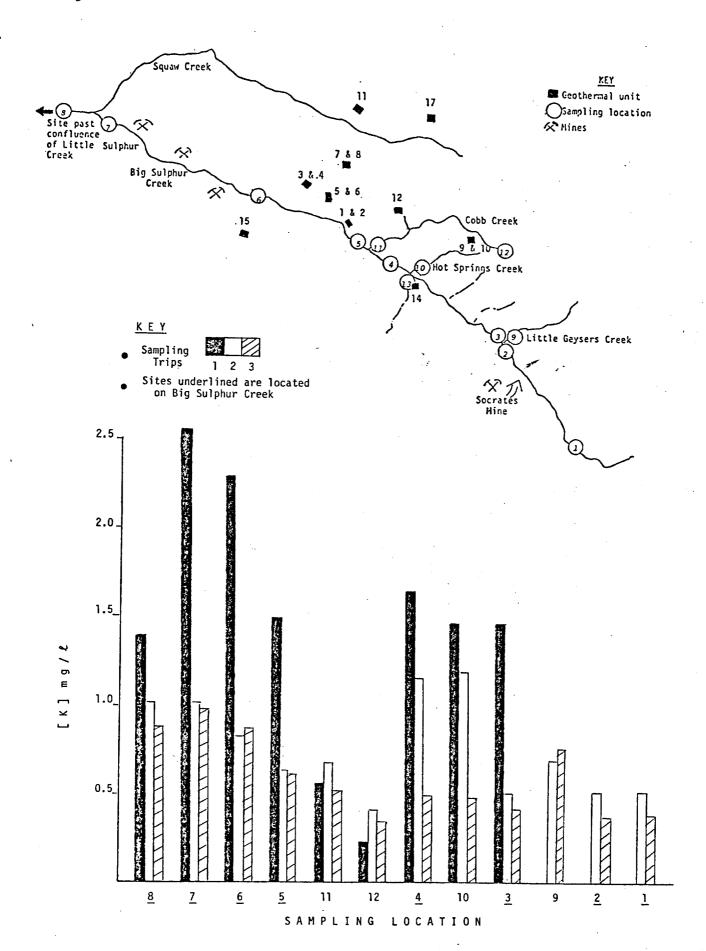


Table 10. Anions. (values in mg/l)

		Sampling Location											
	1	2	3	4	5	6	7	8	9	10	11	12	13
s0 ₄ =													
1. July	*	*	30.0	43.0	45.0	165.0	185.0	34.0	*	52.0	19.0	5.8	*
2. Oct.	8.9	8.2	8.2	38.0	20.0	31.0	50.0	34.5	24.3	80.0	20.0	7.8	26.4
3. Feb.	4.0	27.0	23.0	26.0	24.0	69.4	69.8	32.0	15.0	25.0	12.0	4.8	9.2
<u>C1</u>													
l. July	*	*	4.6	4.0	3.6	13.5	3.15	3.35	*	.3	4.0	1.85	*
2. Oct.	3.7	2.1	.2.3	3.8	2.6	1.6	2.3	3.4	2.4	3.2	3.1	3.2	3.6
3. Feb.	1.9	1.8	1.7	1.9	2.1	1.6	2.4	2.3	1.8	1.9	2.0	1.7	1.9
NO ₃													
l. July	*	*	3.3	4.3	5.7	28.0	37.5	6.0	*	3.0	ND .	ND	*
2. Oct.	1.4	4.0	1.95	20.0	11.0	4.1	8.7	8.5	11.2	6.1	2.4	6.5	6.5
3. Feb.	ND	ND	ND	0.3	0.9	2.8	4.9	2.5	0.6	0.9	1.5	0.9	ND
F ⁻ 3.	-												
3.	0.18	0.05	0.05	0.05	0.07	0.13	0.13	0.10	0.08	0.08	0.13	0.13	0.08

^{*} Indicates no sample collected.

ND = Not detected.

Table 11. Dissolved Trace Elements (Ranges of values in µg/1).

Element	Trip Numl (July		Trip Num (Octobe	ber Two r 1979)	Trip Numb (Februar	
A1	ND -	37.0 (7)	19.7 (11) -	169.2 (6)	ND -	57.9 (7)
As	ND -	134.8 (10)	ND -	100.0 (10)	ND -	95.6 (6)
В	68.0 (12) - 5	5022. (3)	45.4 (1) -	929.9 (11)	27.5 (1) -	1205. (9)
Ca*	18.3 (12) -	52.3 (7)	7.6 (3) -	32.8 (11)	12.3 (1) -	33.5 (7)
Cd	ND	÷	ND -	6.12(10)	ND	
Cu	ND _	5.20(6)	ND -	10.5 (4)	ND	
Fe	ND -	104.4 (3)	12.8 (12) -	227.5 (6)	2.94(12) -	27.9 (9)
K	230.6 (12) - 2	2541. (7)	408.9 (12) -	1159. (4)	349.2 (12) -	984.1 (7)
Li	ND _	48.7 (10)	ND -	35.8 (10)	ND -	10.1 (10)
Mg*	9.3 (12) -	50.2 (10)	9.3 (12) -	50.6 (10)	7.6 (12) -	69.5 (6)
Mn	ND -	162.8 (3)	1.02(12) -	68.6 (9)	ND -	97.4 (9)
Мо	ND -	28.8 (7)	ND -	24.7 (10)	ND -	29.7 (7)
Na*	4.1 (12) -	22.9 (7)	2.3 (3) -	10.9 (10)	2.7 (2) -	7.6 (7)
Ni	ND -	132.2 (4)	ND -	57.8 (4)	ND	30.0 (7)
P	ND -	201.8 (4)	ND -	338.2 (10)	ND -	248.9 (10
Pb	ND		ND -	57.2 (10)	ND -	52.4 (6)
Se	ND		ND -	68.0 (10)	, ND	* *
Si*	6.54(12) -	43.8 (3)	5.76(2) -	30.5 (10)	5.95(12) -	16.6 (9)
Sr	200.6 (12) -	474.6 (6)	59.0 (3) -	380.4 (10)	99.3 (1) -	336.4 (11)
Ti	ND		ND -	4.08(6)	ND	
٧	ND _	3.57(6,7)	ND -	3.29(10)	ND -	3.21(6)
Zn	ND _	9.62 (10)	ND -	31.0 (4)	ND -	23.5 (8)

Parentheses denote sampling location.

Note: Data not collected in July 1979 for sites one, two, and nine.

^{*} = Values in mg/l.

ND = Not detected.

Table 12. Sediment: HCl Extract. Ranges of values in µg/gm dry weight.

Size fraction: Trip number:	850 y - 590 μ		590 μ – 250 μ	
	l; July 1979	2; Oct. 1979	1; July 1979	2; Oct. 1979
Element				
As	27.1(12)-46.6(11)*	ND-8.4(2)	18.3(1)-34.4(5)	ND
В	1.93(12)-7.95(9)	2.06(12)-4.078(2)	1.75(12)-9.61(9)	2.07(12)-3.57(2)
Ca	1198.(1)-6045.(2)	1131.(1)-5529.(2)	1199.(1)-5829(2)	1175.(9)-5434(3)
Fe	1431.(10)-2160(1)	2684.(9)-6739.(13)	1843.(12)-2759.(10)	2744.(9)-7027.(2)
K	40.5(4)-90.9(9)	41.2(1)-99.6(13)	33.0(4)-89.1(9)	43.7(4)-73.8(8)
Li	1.48(1)-3.65(11)	0.88(9)-329(10)	1.14(1)-2.87(10)	0.71(9)-2.78(11)
Мо	2.55(12)-5.41(2)	ND-2.17(2)	2.22(12)-4.84(2)	ND-1.92(2)
Ni	36.0(11)-261.2(1)	30.4(13)-237.(2)	26.3(11)-184.5(2)	28.0(11)-195.1(2)
Pb	11.22(12)-13.88(1)	6.70(5)-12.56(2)	10.8(12-14.4(2)	6.8(11)-12.7(2)
Si	166.(1)-2278.(9)	1440.(7)-2369(10)	1384.(7)-2415(9)	1493.(8)-2298(10)
Sr	8.99(1)-33.29(7)	6.53(1)-32.0(8)	8.9(1)-3.14(8)	6.83(1)-28.9(3)
Ti	8.29(9)-41.37(11)	6.13(9)-31.98(11)	11.0(1)-38.6(11)	6.58(9)-36.1(11)
V	7.40(9)-12.01(11)	7.60(1)-12.96(2)	5.9(1)-11.9(7)	6.88(1)-13.0(2)
Zn	8.90(12)-27.36(9)	10.90)12)-23.9(13)	10.3(12)-35.2(9)	12.1(12)-17.6(2)
		•	5 .	

^{*} Parentheses indicate station number.

ND = Not detected.

Table 13. Sediment: HC1 Extract. Ranges of values in µg/gm dry weight.

Size fraction:	250 μ -	< 149 u		
Trip number:	1; July 1979	2; Oct. 1979	1; July 1979	
Element		W		
As	16.1 (8)- 39.1 (11)*	ND 7.6 (1)	ND - 16.3 (3)	
В	2.3 (12)- 13.7 (9)	2.4 (9)- 4.7. (7)	3.7 (2)- 51.1 (3)	
Ca	1381. (12)- 8643. (8)	1437. (9)- 4808. (2)	2962. (1)- 8690. (8)	
, F _e	1696. (11)- 2120. (6)	2659. (9)- 6407. (7)	3391. (12)- 8705. (6)	
κ	45.3 (4)- \78.9 (8)	43.9 (4)- 71.7 (8)	98.2 (4)- 312.9 (8)	
Li	1.35 (9)- 3.30 (5)	0.77 (9)- 3.19(11)	1.33 (9)- 4.16(11)	
Мо	2.2 (12)- 4.8 (2)	ND - 2.1 (3)	. ND - 10.0 (8)	
Ni	25.6 (11)- 235.2 (1)	34.33(11)- 269.0 (1)	50.4 (11)- 333.1 (3)	
Pb	10.2 (8)- 15.4 (2)	6.7 (9)- 12.2 (1)	12.3 (4)- 26.6 (3)	
Si	1719. (12)- 2672. (9)	1484. (8)- 2467. (10)	1594. (8)- 5526. (6)	
Sr	12.0 (1)- 65.3 (8)	8.79 (1)- 27.74(11)	22.6 (10)- 57.9 (6)	
Ti	7.7 (9)- 34.4 (11)	5.6 (9)- 40.5 (11)	4.7 (9)- 26.2 (11)	
٧	7.2 (12)- 13.1 -(2)	7.6 (9)- 13.2 (11)	14.0 a (8)- 25.0 (3)	
· Zn	10.4 (12)- 41.2 (9)	11.85(12)- 23.07(13)	18.33(12)- 111.1 (3)	

^{*} Parenthesis indicates sampling location.

ND = Not detected.

Table 14. Particulate Trace Elements: HCl Extract (Ranges of values in µg/l filtered).

	Element	Trip Number One (July 1979)	Trip Number Two (October 1979)
	As	ND	ND - 125.4(4)
:	В	0.160(12) - 1.63 (7)	ND - 43.1(4)
	К	ND - 6.97 (6)	ND - 7881.8(4)
	Мо	ND - 0.095(8)	ND - 16.3(4)
	Pb	ND - 0.478(7)	ND - 94.8(4)
	Ti	ND - 0.112(6)	0.133(12) - 274.2(4)
	V	ND - 0.115(7)	0.181(8) - 75.9(4)

Parentheses indicate sampling location. ND = Not detected.

Table 15. Composition of Unit 12 Cooling Water; June 28, 1979. (Values in mg/1)

	3:20 pm	6:10 pm	
Cations: *			
As	0.06	0.03	
В	77.4	82.3	
Fe	29.6	25.9	
Mn	1.04	0.65	
P	0.14	0.17	
Pb	0.04	0.05	
Zn	0.08	0.04	
Ca	1.46	7.75 💉 🔑	
K	68.8	284.0	
Mg	0.28	0.42	
Na	4.45	7.91	
Anions: **			
F	0.55	N.D.	
C 1	10.0	6.8	
so ₄	1425.0	700.0	

^{*} Analyzed by inductively coupled argon plasma spectroscopy.

^{**} Analyzed by anion chromatography.

ND = Not detected.

DISCUSSION

Some preliminary elemental data is presented on the dissolved and particulate components of the water column and on the sediments. An important point to emphasize is that the results are preliminary. In order to fully evaluate the water data, it must be normalized to account for varying flow.

Trip number one was taken in the summer when the flow rate was very low. As a result, we did not collect samples from sites one, two, or nine. Sites one and two were merely pools of standing water, therefore not representative of normal conditions. Site nine was omitted since the flow of Big Sulphur Creek at this time was entirely from Little Geysers Creek. Essentially, site three can be considered equal to site nine. Any difference might be accounted for by substrate difference or subsurface flows.

During trip two there were intermittent heavy rains. The streams are very responsive to rainfall and our flow rates during the sampling week fluctuated greatly. Rainfall was not a problem during trip three although the flow was rapid due to groundwater recharge.

with these varying flows, it is very difficult, at this stage, to compare one quarter to another. It is also difficult to ascertain the mass loading of elemental concentrations between sites until we standardize the data. We do have our own flow data at each sampling location. Additionally, we are obtaining rating curves for the total continuous flow of Big Sulphur Creek from P.G.&E. and DWR.

Nonetheless, some general trends do stand out. In many cases, there is an increase in a constituent in Big Sulphur Creek immediately after a tributary, reflecting the concentration in that tributary. However, site five is fairly low even after the upstream additions. It is seen that values often increase after the main stream passes the area of major development at site six, stay high

through site seven (a distance of several miles), then decrease at site eight due to dilution from Squaw Creek and Little Sulphur Creek.

The following are a few interesting observations on the water data.

- 1.) Ammonia values, though receiving high input from Hot Springs Creek, remain low until sites six and seven where peak values are seen.
 Often the water quality criterion for unionized NH₃ is exceeded.
 This value as recommended by the EPA (EPA, 1976) is 0.02 mg/l.
 Ammonia is also a major constituent of cooling tower water.
- as ten). Sulfate is the largest constituent of cooling tower water (Koranda, 1980). It is interesting to note that Cobb Creek more than doubles in value during its course to Big Sulphur. Cobb Creek is not a thermal creek, but originates as a clean spring near the ridge line. It is also a portion of the watershed which receives cooling tower drift from units nine, ten, and twelve.
- 3.) Chloride does not appear to have a trend though there is an increase in site six during the summer. Otherwise, chloride does not appear to be enriched in any location.
- 4.) Nitrate values appear to be scattered. A possible input to Big Sulphur may be a result of the hydroseeding done for erosion control.
- 5.) Aluminum values are higher at site six and seven. Tributaries nine and ten are approximately equal.
- 6.) Arsenic values are high at site ten. There appears to be a slight increase from site four through six.

- 7.) Boron is very high at site nine and this is reflected in site three. Site ten is also high. However, sites three to five are relatively constant, and values rise at site six. Boron is a major constituent in the cooling tower water. The increase between site twelve and eleven may reflect cooling tower drift.
- 8.) Fe and Mn values appear to be elevated at site nine, then decrease, then rise again at site six. Fe has contradictory values but a flow adjustment would perhaps aid the interpretation. Fe values increase in all three quarters from site twelve to site eleven.
- 9.) Potassium is another major constituent of cooling tower water and natural geothermal water. A high value is observed at nine, then a continuous increase from site three to seven. Values also appear to increase down Cobb Creek.
- 10.) Li exhibits a large difference in concentration between the two thermal tributaries. Site ten is always much higher in value. Perhaps Li may be of future value to us as a geochemical marker.
- 11.) Pb, Ti, V, and Mo are all present at elevated levels in Hot Springs Creek. It is observed that they generally remain constant through sites six and/or seven. In most cases, the values are below the detection limit. As a footnote, vanadium pentoxide is a compound utilized by the Stretford process for H₂S abatement.
- 12.) Ca and Sr display similar tendencies. Both achieve peak values at site seven or site eleven. In all cases, there is a signficant increase in values down Cobb Creek.

Observations on HCl sediment extract.

- 1.) As and Mo appear to have somewhat uniform distributions in the watershed. Peak values for As seem scattered. Mo is shown at high concentration often at site two. Their concentrations are both definitely enriched by input from site nine. Another common trait they share is that both appear to be removed quickly by the natural flushing of the rain between July and October.
- 2.) In low flow periods, B achieves a peak value at site nine in each fraction. Values even out between sites three and five, then increase from six through eight. After the fall rains, B tends to show constant background levels. Site nine always appears to be significantly higher in extractable B than site ten.
- 3.) Potassium follows the same trends as in the water data. It is at its highest value in either site nine or eight and always lowest at site four. The high value at nine is what we would expect from the water data. High values at site eight may reflect the different geochemistry of the two streams, Squaw Creek and Little Sulphur Creek, which enter between sites seven and eight. Another possibility is that it may also reflect the differences in vegetation between the drainages.
- 4.) Li exhibits some unusual traits. Lowest values are seen in the upper reaches of the watershed at sites one, two, nine, and three. Highest values are always at site ten, eleven, and five.
- 5.) Sr, Ca, and perhaps V lead one to speculate that the origin of their distributions might be attributed to leachings from the

- abandoned mine tailings. Low values at one increase to high values at two or three with nine contributing little input. Likewise, increases from six to seven implicate this type of input.
- 6.) Pb and Ni also show similar patterns to the above elements in (5).

 Pb and Ni do not appear to correlate with any geothermal areas.

 Highest values are attained in the upper Big Sulphur Creek area, sites one and two, and lowest are found in Cobb Creek, sites eleven and twelve.
- 7.) Si and Zn, however, appear to correlate strongly with the geothermal areas. Highest values are seen in nine and ten, the lowest values in the comparatively "clean" stations one and twelve.
- 8.) Ti appears to exhibit contrary behavior to the above elements. It normally is found at its highest value at site eleven, and lowest in site nine. Ti seems to be ubiquitous within the watershed in fluctuating concentrations.

Particulate trace elements.

- 1.) B and K follow a familiar pattern. Both register high values in nine which carries into site three. A slow decrease follows through site five, then a signficant rise in values occurs at sites six and seven. By site eight, dilution has reduced the concentration.
- 2.) In low flows, As and Mo are generally undetectable. This may reflect their affinity for the sediment or their easy mobilization downstream in higher flows as previously mentioned.
- 3.) Pb and V are found in highest concentration at site seven which may lead credence to the theory that mine tailings are a significant contributor.

4.) One might notice that all peak values for the July trip occur from sites six to eight. This shouldn't be surprising since the greater flow in the lower sampling sites keeps the particulates more suspended and they are less able to settle. A graphic illustration of the ability of higher flows to mobilize tremendous amounts of trace elements is shown in the October trip. All peak values are shown at site four. It is not merely coincidental that our sampling there was conducted in a downpour while the stream was rising rapidly.

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CONCLUSION

The data presented have shown there are some observable trends with regard to several geothermal related constituents along the path of Big Sulphur Creek. Concentrations of ammonia, boron, potassium, and sulfate are all found in elevated levels in the two thermal tributaries, Hot Springs Creek and Little Geysers Creek. Big Sulphur Creek appears able to absorb these inputs with steady state values or slight increases. However, we have seen that upon passing the area of major development, a significant rise in concentration appears. Since these four constituents are also found in high levels in cooling tower waters, it seems evident that the geothermal operations are contributing to the aquatic environment. As secondary evidence, we have seen in several cases that concentrations of drift related constituents have increased in Cobb Creek. Cobb Creek originates as a clean, springfed creek and is exposed in its lower portion to cooling tower drift from Units 9, 10, and 12.

Our data, having not been corrected for varying flow rates, show the concentration of elements in the water column at a given time. What is not shown is the mass input from the different sources, i.e., the additive net contribution from these sources. Nonetheless, one can appreciate that the region of low-level exposure is extensive when one considers the size of the watershed. Since Big Sulphur Creek is a major tributary of the Russian River, there is evidence for concern as to its impact upon recreation areas, irrigation waters, and fisheries.

The data also show that a definite need exists for our type of study in other areas of commercial geothermal expansion. The most likely candidate is the Upper Putah Creek watershed. New units 13 and 16 are in varying stages of development and should be generating power by the end of 1980 or early 1981. With our expanded data base, current methodology and knowledge of the

geochemical processes involved in the area, we feel we can better evaluate the environmental effects of geothermal development upon this watershed. This data will also serve as an extremely useful tool in recommending or assessing the efficiency of any mitigation procedures.

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STATEMENT OF PURPOSE

Geysers-Calistoga KGRA Water Quality/Biology Monitoring

INTRODUCTION

The rapid development of geothermal resources in The Geysers-Calistoga Known Geothermal Resource Area (KGRA) has led to many aquatic monitoring programs designed to meet many different development and regulatory purposes. Presently, power plant developers, steam suppliers, and local, state, and federal regulatory agencies have mostly separate and uncoordinated water quality and aquatic biology programs and requirements. Various programs including baseline studies, routine monitoring, and special investigations, are presently underway or planned in the near future. With so many programs having such divergent purposes, producing a realistic picture of geothermal development impacts is difficult. Additionally, use of the collected data to plan additional development, to meet regulatory needs, and to assess the effectiveness of aquatic mitigation and protection programs has not been efficient or cost-effective.

These complex problems and the concurrent need by developers and regulators to collect useful data have resulted in many of these entities meeting to determine if a more efficient and cost-effective approach was possible. The following parties have met to discuss the monitoring problems:

California Energy Commission
Pacific Cas and Electric Company
California Regional Water Quality Control Board,
Central Valley and North Coast Regions
California Department of Fish and Came
California Department of Water Resources
Union Oil Company
Aminoil USA Inc.
U.S. Geological Eurvey
Lawrence Livermore Laboratory

These parties met on August 16, September 27, and October 16, 1979, to discuss the needs and objectives for a combined and cooperative program. The participants at these meetings were concerned that the program be designed to satisfy regulatory needs and be agreed to by the involved parties. Therefore, they decided to prepare this statement to outline the program's concepts for distribution to the developers, regulatory agencies, and others involved in The Geysers-Calistoga KGRA.

PRINCIPLES OF THE PROGRAM

Objectives

Using or modifying existing monitoring programs, the programs will be designed:

- To evaluate cumulative impacts on aquatic resources due to full-field geothermal development, as well as other types of development, in the steam-dominated portion of The Geysers-Calistoga KGRA,
- To evaluate the effectiveness of measures used to protect aquatic resources from the impacts of developing power plants, steam fields, and roads in the steam-dominated portion of The Geysers-Calistoga KGRA,
- To coordinate ongoing and proposed monitoring programs in The Geysers-Calistoga KGRA in order to reduce redundancy, to reduce unnecessary financial and personnel expenditures, to promote flow of information among interested agencies and persons in the KGRA.

Use of Information

 As this program develops into a regional monitoring program, it will replace, where practicable, site-specific post-development monitoring programs required by regulatory agencies. Also, where practicable, it will provide and/or augment baseline data in undeveloped areas needed to prepare plans for proposed power plants and steam fields. However, data collected from the program may not apply to areas outside the program's boundaries. In such areas, site-specific predevelopment baseline studies are recommended. The program can be modified to include these new areas as they begin to be explored and developed.

Monitoring Program Design

• The monitoring program will be designed with input from the cooperating parties, using inhouse technical expertise to the extent possible. The final monitoring program will be agreed to by all parties at the appropriate management level.

Funding

• Each participating entity will provide support to the program through direct funding, capital equipment, support personnel, or some combination. The details of the participation will be negotiated after the specific program elements and schedule are proposed. A method for funding by new participants will be provided.

DISCUSSION

The above principles, if implemented in a joint program, will provide a well-structured, integrated approach for evaluating continuing geothermal

development. This concept will provide substantially more information than is currently available at reduced cost to the individual party. Significant benefits that can be designed into such a program include:

- Reduction of the study area to key areas where generic impacts of development can be monitored.
- Standardization of sampling and analysis methods to allow valid comparisons between projects.
- Simplification of study design and scope to address needed information for the entire study area rather than limited site-specific evaluations.
- Coordination of data to provide better communication and more rapid distribution of key findings to all concerned.
- Protection of additional aquatic habitat not presently evaluated due to project boundaries or uncertain political jurisdiction.

CONCLUSION

A joint aquatic monitoring program designed with the purposes and objectives stated above will provide substantial benefit to those parties concerned with geothermal development in The Geysers-Calistoga KSRA. Producing such a program will require the concurrence and support of all those directly concerned with geothermal development in The Geysers-Calistoga KGRA. Such a coordinated approach will provide for the needs of those groups with responsibilities for controlling operational processes, environmental protection/mitigation programs, regulatory requirements, research projects, environmental document preparation, regulatory hearing preparation, and resource planning. All these benefits will accrue at reduced capital and personnel costs.

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